# CASE FILE

## NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3884

IGNITION DELAYS AND FLUID PROPERTIES OF SEVERAL FUELS

AND NITRIC ACID OXIDANTS IN TEMPERATURE RANGE

FROM 70° TO -105° F

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IGNITION DELAYS AND FLUID PROPERTIES OF SEVERAL FUELS AND NITRIC

ACID OXIDANTS IN TEMPERATURE RANGE FROM 70° TO -105° F<sup>1</sup>

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#### SUMMARY

Ignition-delay characteristics of approximately 90 fuel-oxidant combinations were determined in a modified open-cup apparatus at  $-40^{\circ}$  F. Combinations considered worthy of further study were investigated at temperatures in the range from  $70^{\circ}$  to  $-105^{\circ}$  F. Freezing temperatures of acids were determined as well as viscosities of several fuels at moderate and low temperatures.

At  $-40^{\circ}$  F, several blends of aromatic amines with triethylamine show promise as ignitor fuels with mixed acid (nitric acid plus sulfuric acid) and red fuming nitric acid, and some of these fuels may be useful also with white fuming nitric acid.

Several blends of aromatic amines in triethylamine were found to be fluid at -105° F, and red fuming nitric acid containing approximately 3 percent water and 19 percent nitrogen tetroxide was found to freeze at approximately -87° F. With this acid, 30 percent by volume blends of o-toluidine, aniline, and xylidines, respectively, in triethylamine showed desirable ignition characteristics at -76° F, specified maximum freezing temperature for military aviation fuels. With this red fuming nitric acid supercooled to -105° F, 30 percent by volume o-toluidine in triethylamine showed the most consistent ignitibility.

#### INTRODUCTION

Fully extended tactical applications of rocket powerplants require fuel-oxidant combinations that are fluid and self-igniting at very low temperature. A primary use for these fuel-oxidant combinations will

<sup>&</sup>lt;sup>1</sup>Supersedes NACA Research Memorandum E51Jll, "Ignition-Delay Characteristics in Modified Open-Cup Apparatus of Several Fuels with Nitric Acid Oxidants within Temperature Range 70° to -105° F", by Riley 0. Miller, 1951.

NACA TN 3884

be in booster rockets for aircraft flying at high altitudes because repeated starts will be required and each start must be quick and reliable. Reliable low-temperature starts will be required also of air-to-air and air-to-surface rocket missiles, and rockets used under artic conditions.

For economic and logistic reasons, nitric acid oxidants are favored for rocket applications in which propellants are to be stored several months. Mixed acid (nitric acid plus sulfuric acid), red fuming nitric acid (nitric acid plus nitrogen tetroxide), and white fuming nitric acid have been used for this purpose. Earlier investigations at the Lewis laboratory (refs. 1 and 2) and elsewhere have shown that several fuels will ignite with mixed acid at temperatures of  $-40^{\circ}$  F and lower. Mixed acid, however, has the disadvantage of possible sludge formation during storage; other types of nitric acid may therefore be preferred. The early experiments, however, showed that certain fuels which ignite with mixed acid at  $-40^{\circ}$  F do not ignite satisfactorily with other acids at this temperature. A further investigation of ignitor fuels for use with several types of acid at  $-40^{\circ}$  F was therefore in order.

The temperature  $-40^{\circ}$  F has been used by several investigators as a standard low temperature for ignition-delay experiments and may be low enough as a minimum starting temperature for certain rocket applications. Lower temperatures, however, have been specified for military aircraft fuels and equipment. The freezing temperature for several military jet-propulsion fuels is currently specified in references 3 and 4 to be not higher than  $-76^{\circ}$  F ( $-60^{\circ}$  C), and a minimum design temperature of  $-103^{\circ}$  F ( $-75^{\circ}$  C) is recommended in reference 5 because of very low temperatures occurring at high altitude in tropical regions. A need for investigation of fluid properties and ignition characteristics of fuel-oxidant combinations at temperatures at least as low as  $-76^{\circ}$  F was apparent.

The investigation, described herein, was conducted at the NACA lewis laboratory in 1951 to select (a) fuels that are fluid at low temperatures and will ignite at  $-40^{\circ}$  F with mixed, red fuming, and white fuming nitric acids; and (b) a nitric acid oxidant that has a final freezing temperature that is lower than  $-76^{\circ}$  F and will ignite several low viscosity fuels at  $-76^{\circ}$  F and lower. Fuels were investigated with a view toward their utility either as rocket propellants or as ignitor fluids to initiate combustion of hydrocarbon fuels with an acid oxidant which could be used as a propellant in either case.

The viscosities of 24 fuels, the approximate freezing temperatures of 16 acids, and the ignition-delay characteristics for 93 fuel-oxidant combinations are presented herein. Ignition-delay data were obtained in a modified open-cup apparatus similar to that described in reference 2 except that improved instrumentation was incorporated.

#### OXIDANTS AND FUELS

#### Oxidants

Several mixed, red fuming, and white fuming nitric acids were investigated. The approximate freezing temperatures, compositions, and histories of these oxidant acids are presented in table I.

A code system is used herein to designate the several acids. letters of the code symbol indicate the type of acid, that is: MA, mixed acid; RFNA, red fuming nitric acid; WFNA, white fuming nitric acid. The first number in the symbol always indicates the approximate percentage of water and the second number (when used) indicates the approximate percentage of either sulfuric acid in mixed acid or nitrogen tetroxide in red fuming nitric acid. Thus the symbol MA-2-17 designates a mixed acid with 2 percent water and 17 percent by weight sulfuric acid; RFNA-3-19, a red fuming nitric acid with approximately 3 percent water and 19 percent nitrogen tetroxide; and WFNA-7, a white fuming nitric acid with 7 percent water. Several special white fuming nitric acids containing other additives were also used. For these acids, the percentage of additive, indicated by a number, and the chemical symbol of the additive are given in parentheses following the basic symbol; thus, WFNA-8(6-KNO3) is a white fuming nitric acid containing 8 percent water and 6 percent potassium nitrate. Three lots of red fuming nitric acid containing 2.2 to 3.0 percent water were designated RFNA-3-19 and the lot is indicated in several instances as lot a, b, or c, respectively.

#### Fuels

In most of this investigation fuels were used that were blends of aromatic amines in triethylamine. Data were also obtained using blended or unblended furan compounds, mercaptans, various unsaturated compounds, and hydrazine hydrate. The purpose of blending was (a) to produce fuels which were more fluid than the active component alone; and (b) to investigate further the possibility of producing blends with desirable ignition characteristics, inasmuch as certain blended fuels have been shown to ignite more satisfactorily than the parent constituents (refs. 2 and 6).

The Shell Development Company supplied the following compounds: allyl glycidyl ether, 2-methylpentadiene, 2,2,4,6-tetramethyldihydropyridine, 3-mercapto-1-propanol; they also furnished physical-chemical data. The mixed butyl mercaptans and N,N-diallylaniline were supplied by the California Research Corporation through an arrangement with the Bureau of Aeronautics, Department of the Navy.

#### PROCEDURE AND APPARATUS

The experimental work may be divided into two phases, (a) measurement of physical and chemical properties of propellants, and (b) measurement of ignition delays of fuel-oxidant combinations.

#### Measurement of Physical and Chemical Properties

Analysis of acids. - Red fuming, white fuming, and anhydrous nitric acids were analyzed according to the method of reference 7. Sulfuric acid in mixed acid was determined as barium sulfate. The compositions of several acids were calculated from the quantities of material added to the acid and notation has been made in such cases (see table I).

Freezing temperatures of acids. - Approximate freezing temperatures of acids were obtained by first freezing 20 milliliters of the acid in a thick walled 1- by 8-inch test tube, and then slowly warming the acid and noting the temperature at which cloudiness disappeared. A total-immersion toluene thermometer was used to measure temperatures and was calibrated under the conditions of the experiment with a standard iron-constantan thermocouple.

Viscosities of fuels. - Viscosities of fuels were obtained by a modified Ostwald viscosimeter according to the method of reference 8. Viscosities for most of the fuels were determined at  $-40^{\circ}$  F and viscosities for several fuels showing desirable ignition characteristics were also determined at  $77^{\circ}$  F and at temperatures between  $-103^{\circ}$  and  $-113^{\circ}$  F.

#### Measurement of Ignition Delay

Apparatus and method. - Except for improvements in instrumentation, the apparatus, which is shown in figure 1, is the same as that described in reference 2. The function of the apparatus was to bring the fuel and oxidant into contact with each other at a desired initial temperature and to measure the time interval between the start of mutual contact and the first appearance of flame. This time interval was defined as the ignition-delay interval. One milliliter of the fuel was contained in a small pyrex glass ampule submerged in 3 milliliters of the acid oxidant in a 1- by 8-inch pyrex ignition-type test tube. Both the fuel and oxidant were cooled to a desired temperature by submersing the test tube in a constant-temperature methanol bath contained in a clearglass Dewar cylinder. The fuel ampule was broken by a stainless-steel rod that was struck by a falling weight. High-speed motion pictures (ref. 2) show that the ampule is broken and the fuel and oxidant contact each other within an interval of less than 2 milliseconds. The extent of mixing probably varies somewhat as a result of individual

differences in ampules and viscosities of propellants. The insulated weight closed an electric circuit which provided a starting signal for the timing instruments at the moment the ampule was broken.

Two types of instrument actuated by light emission were used simultaneously to measure the delay interval. Instantaneous indications were obtained from an electronic timer started through a thyratron relay circuit triggered by the starting signal and stopped by an amplified signal caused by light from the test tube striking a photocell. Continuous records of light emission against time were also obtained by means of a camera oscillograph. The recorded signal was a 2000-cycleper-second carrier wave modulated by the output of a photocell. The start of the ignition-delay interval on the oscillograph record was indicated by a signal from an argon bulb near the photocell which was shorted out by a thyratron when the falling weight made electric contact with the rod. Another channel on the oscillograph was used to record the amplified output of a microphone which was about 1 foot from the apparatus; an indication of pressure fluctuations during the reaction of the propellants was thus obtained simultaneously with the light emission record.

Unless otherwise noted, the ignition data reported herein were obtained from the oscillograph records. The electronic counter was used to monitor and check the results, and the microphone record also served as an auxiliary indication of the start of the ignition-delay interval and a secondary check on the start of ignition.

Interpretation of records. - Illustrative examples of the oscillograph records from a series of experiments giving good reproducibility and a series giving wide variations are shown in figures 2 and 3, respectively. In figures 2(a) and 2(b) are shown light-emission and sound records, respectively, from four experiments with 30 percent aniline plus 70 percent triethylamine and a red fuming nitric acid at -76° F. The vertical bars are timing marks, 10 milliseconds apart. The light-emission-record number 1 (fig. 2(a)), for example, is interpreted as follows: The width of the carrier signal represents the intensity of light striking the photocell. The start of the ignitiondelay interval is indicated at A by the sharp decay of the signal due to the extinguishing of the argon pilot light by the weight striking the rod. At B (25 millisec) the first of several short rapid flashes occurred but continuous flame did not start until C (37 millisec). In the intervals D to E and F to G the photocell was saturated with strong light. The saturated intervals are identified by the carrier signal being less than the ground level as in the interval between A and B. The records of experiments 2 and 4 were obtained with a different photoelectric pickup than those of experiments 1 and 3 and the quality of the signal was less satisfactory. The irregular

fluctuations during the first parts of records from experiments 2 and 4 (fig. 2(a)) were attributed to microphonic pickup and were not defined as flashes. Flashes were indicated by very sharp short disturbances of the signal.

The sound records obtained simultaneously are shown in figure 2(b). The validity of the start signal A of experiment 1 (fig. 2(a)) is confirmed by the sound record (experiment 1, fig. 2(b)), which starts to become fuzzy (indicating noise) at the same instant A within an interval of the order of 1 millisecond. At C (fig. 2(b)), 37 milliseconds from the start of the noise, a strong pressure pulse is indicated by a dip in the sound record and corresponds to the start of the continuous interval of light emission (fig. 2(a)). The remainder of the sound record is difficult to interpret because signals from vibrations of the flame are probably mixed with those from mechanical vibrations of the hood in which the experiments were conducted. The ignition-delay intervals as determined by the electronic timer, the times of short flashes and the starts of continuous flames as indicated by the light-emission records (fig. 2(a)), and the first strong pressure pulse from sound records (fig. 2(b)) are shown in the following table:

Experiment	Ignition delay from electronic timer, millisec	Time of short flashes, millisec	Start of first con- tinuous flame, millisec	Start of first strong pressure pulse, millisec
1	1 24 2 34 		37	37
2			<b></b> 37	34
3	38	38	38	36
4			38	38

The ignition-delay intervals as determined by the electronic counter varied from 24 to 38 milliseconds, because the counter was stopped during experiments 1, 2, and 4 by short flashes of light, instead of by the start of continuous flame. The starts of the continuous flames were in close agreement, varying between 37 and 38 milliseconds, and these data were accepted as the ignition-delay intervals.

Figure 3 shows oscillograph records for 30 percent xylidine plus 70 percent triethylamine with red fuming nitric acid at -87° F, and represents a series of records which were more difficult to interpret than those in figure 2. The light-emission record of experiment 1 shows short rapid flashes starting at B (114 millisec) and start of continuous flame at C (128 millisec). The record of experiment 2. however, shows only a momentary weak flame at C and the gradual start of continuous flame at D (175 millisec). The record of experiment 3 shows D to be the start of a series of weak flames with stronger flames occurring at E (330 millisec) and F (390 millisec). In record 3, D was accepted as the start of ignition because it indicates the start of a series of weak flames corresponding to the first strong continuous flame on record 2. Figure 3 also shows unusually large deviations between the light-emission records and the sound records: the sound records were disregarded. Although occasionally, as in experiments 2 and 3 (fig. 3), selection of the ignition-delay interval was somewhat arbitrary, the numerical data in such instances nevertheless indicate trends.

The data of figure 3 also illustrate the fact that ignition in some cases appears to be a periodic process. Variations in data may thus be a function of the fuel and oxidant used and the extent of mixing. The periodic process possibly may be affected also by surface conditions and trace impurities.

#### RESULTS AND DISCUSSION

Fluid Properties of Fuels and Oxidants at Low Temperatures

The use of a liquid rocket propellant at low temperature may be limited by either freezing or excessive viscosity.

Freezing temperature of acid oxidants. - Freezing, rather than viscosity, limits the fluidity of acid oxidants at low temperatures. Approximate freezing temperatures of most of the acids used in this investigation are presented in table I. Acids investigated which had freezing temperatures lower than -76° F were a mixed acid containing 29 percent sulfuric acid (MA-0-29), red fuming nitric acids containing approximately 3 percent water and 16 and 19 percent nitrogen tetroxide (RFNA-3-16 and RFNA-3-19), a white fuming nitric acid containing 9 percent water (WFNA-9), and nitric acids containing 8 percent or more water and potassium nitrate or perchloric acid [WFNA-8(6-KNO3), WFNA-9(7-HClO4), and WFNA-11(4-HClO4)]. The acids also showed tendencies to supercool, and it was possible to obtain ignition-delay data with RFNA-3-19 at temperatures as low as -105° F. The tendency for these acids to supercool may constitute an emergency safety factor of practical importance.

Viscosities of fuels. - Kinematic-viscosity - temperature data within the range from 77° to -113° F for several aromatic amines, triethylamine, and blends of aromatic amines with triethylamine are presented in figure 4. The kinematic-viscosity and temperature scales are similar to those recommended by the A.S.T.M. for use with petroleum products. The data for each of the amine fuels are shown to fall close to a straight line, thereby following the relation (ref. 9)

$$log log (v + c) = A log T + B$$

where

y kinematic viscosity, centistokes

c constant, ~ 0.6 to 0.75

T absolute temperature, OR

A,B constants, functions of fuel

The blends of secondary and tertiary aromatic amines were more fluid (less viscous) at low temperatures than the corresponding blends of primary amines. Eight blends are shown in figure 4 to have kinematic viscosities less than 10 centistokes at  $-40^{\circ}$  F and less than 500 centistokes at  $-105^{\circ}$  F.

The blends, apparently, are nonideal solutions. If the solutions were ideal, the kinematic viscosity for a blend could be calculated as

$$v = \frac{1}{(\rho_A v_A + \rho_B v_B) \left(\frac{x_A}{\rho_A v_A} + \frac{x_B}{\rho_B v_B}\right)}$$

where

 $^{\nu},^{\nu}_{A},^{\nu}_{B}$  kinematic viscosities of blend, component A, and component B, respectively, centistokes

 $\rho_A, \rho_B$  densities of components A and B, respectively

 $V_A, V_B$  volume fractions A and B, respectively

 $\mathbf{X}_{\mathbf{A}}, \mathbf{X}_{\mathbf{B}}$  mole fractions A and B, respectively

For several blends, calculated and observed kinematic viscosities are shown in the following table:

Aromatic amine	Percent a		Viscosity, centistokes								
	triethyla	mine		70° F			-40° F				
			Calcu- lated	Observed	Ratio, observed calculated	Calcu- lated	Observed	Ratio, observed calculated			
Aniline	50 30	60 40	0.96	1.72	1.8						
o-Toluidine	50	56 36	0.90	1.57	1.7						
N-Ethylaniline	50 30	53 32	0.79	1.08	1.4	2.03	7.40	3.7			
N,N-Diethylaniline	50 30	47 27	0.74	0.98	1.3	1.84	3.75 2.18	2.0			
N, N-Diallylaniline	50	44	0.72	1.08	1.5	1.74	4.92	2.8			

The observed viscosities are higher than those calculated, especially at low temperature, thereby indicating probable presence of complexes between the components of the blends (ref. 10).

#### Ignition Study of Acid Oxidants at -40° F

Early in the investigation a 50 percent by volume blend of xylidines in triethylamine (suggested by ref. 11) was found to be fairly fluid at  $-40^{\circ}$  F and ignited reproducibly with concentrated white fuming and anhydrous nitric acids. This blend was therefore selected as a reference fuel to study the comparative ignitibility at  $-40^{\circ}$  F of several acids. Some of the acids were also investigated with a 50 percent by volume blend of N,N-diallylaniline in triethylamine. The results of this investigation of acid oxidants are shown in table II.

Acids giving short ignition delays. - As shown in the following table, a mixed acid, several red fuming nitric acids, and white fuming nitric acids containing 2 percent or less water gave short average ignition-delay intervals at -40° F with the two fuels:

Acid	freezing	Average ignition-delay interval at -40° F millisec						
temperature of acid, of	50 Percent xylidine in triethylamine	50 Percent N,N-diallylaniline in triethylamine						
MA-2-17	-68	28	27					
RFNA-3-16	-82	31	28					
RFNA-3-19 (lot a)	<b>-</b> 87	31	26					
RFNA-3-29	-68	31						
RFNA-5-35		34	51					
NA(anh)-0-3	<b>-</b> 45	34	17					
WFNA-2	-45	42	20					

Effect of water in white fuming nitric acid. - With white fuming nitric acids the average ignition delays of the two fuels increased with increase of water in acid as shown by the following table:

Acid	Water in acid,	Average ignition-delay interval at -40° F millisec						
0		50 Percent xylidine in triethylamine	50 Percent N,N-diallylaniline in triethylamine					
NA(anh)-0-3 WFNA-2 WFNA-7 WFNA-9	0.3 1.8 6.8 8.7	34 42 114 No ignition	17 20 No ignition					

Other acids containing 8 percent or more water, WFNA-8(6-KNO $_3$ ), WFNA-9(7-HClO $_4$ ), and WFNA-11(4-HClO $_4$ ), did not ignite. Similar trends were observed with NA(anh)-0-3, WFNA-2, WFNA-7, and WFNA-11(4-HClO $_4$ ) in a 50-pound-thrust rocket chamber (ref. 12).

Effect of ammonium nitrate in white fuming nitric acid. The acids  $\overline{\text{WFNA-2}(5-\text{NH}_4\text{NO}_3)}$  and  $\overline{\text{WFNA-2}(10-\text{NH}_4\text{NO}_3)}$ , prepared by addition of 5 and 10 percent ammonium nitrate to  $\overline{\text{WFNA-2}}$ , were found to ignite 50 percent xylidine in triethylamine with average delays of two to three times those obtained with  $\overline{\text{WFNA-2}}$  alone. This may be the result of the suppression of nitronium  $(\overline{\text{NO}_2}^+)$  and nitrosonuim  $(\overline{\text{NO}^+})$  ions by the nitrate ion. The possible roles of  $\overline{\text{NO}_2}^+$  and  $\overline{\text{NO}^+}$  is discussed in reference 13.

Ignition by low-freezing acids. - A comparison of average ignition-delay intervals at -40° F for several acids freezing below -76° F (-60° C) is shown in the following table:

Acid	Approximate freezing temperature	Average ignition-del	ay interval at -40° F, isec
of acid, of		50 Percent xylidine in triethylamine	50 Percent N,N-diallylaniline in triethylamine
RFNA-3-19	-87	31	26
(lot a)			
RFNA-3-16	-82	31	28
MA-0-29	-87	48	67
WFNA-9	-81	No ignition	
WFNA-8(6-KN03)	<b>-</b> 96	No ignition	
WFNA-9(7-HClO <sub>4</sub> )	-78	No ignition	
WFNA-11(4-HC104)	-91	No ignition	

Because of low freezing temperature and short average ignition delays, acids of the type RFNA-3-19 were used for further ignition experiments at several temperatures.

#### Ignition Study of Fuels at -40° F

A study was made at -40° F to determine the ignitibility of several fuels with representative acids having vigorous and mild ignition characteristics, respectively. The fuels were first investigated with (a) mixed acid, inasmuch as references 1 and 2 show that mixed acid has desirable low-temperature ignition characteristics, and (b) white fuming nitric acid to show their ignitibility with a less vigorous igniting acid. The acids MA-3-17 and WFNA-7 were used for most of these experiments.

Several of these fuels were also investigated with two acids found to have low freezing temperatures (table I), namely, (a) RFNA-3-19, freezing at -87° F and showing desirable ignition characteristics, and (b) WFNA-9, freezing at -81° F. In preliminary experiments (table II) WFNA-9 was unsatisfactory as an igniting acid, but it may be a desirable propellant on the basis of handling and is representative of white fuming acids with freezing temperatures depressed by addition of water.

Ignitibility of blends of aromatic amines in triethylamine. - As shown in table III, with the mixed acid MA-2-17 blends of the aromatic amines, aniline, N-ethylaniline, N,N-diethylaniline, N,N-diallylaniline, o-toluidine, and xylidines, respectively, in triethylamine ignited at  $-40^{\circ}$  F with most of the average delays between 28 and 48 milliseconds and no average greater than 65 milliseconds. With the white fuming nitric acid containing 7 percent water (WFNA-7), all the investigated blends of aromatic amines in triethylamine (except 50 percent N-ethylaniline and 50 percent N,N-diallylaniline, respectively) ignited at  $-40^{\circ}$  F with average delays ranging from 23 to 115 milliseconds.

Ignition of blends of aromatic amines in triethylamine by low-freezing acids. - The investigation with low-freezing red fuming nitric acids (RFNA-3-19) and low-freezing white fuming nitric acid (WFNA-9) at -40° F (table III) showed that the blends of aromatic amines in triethylamine ignited much more satisfactorily with the red fuming acid; the average delays with RFNA-3-19 were between 20 and 55 milliseconds, but with WFNA-9 most of the ignitions were sporadic or did not occur and the average delays were all greater than 100 milliseconds. In these experiments blends of 50 percent aniline and 30 percent xylidines, respectively, in triethylamine showed the most consistent ignitibility with WFNA-7 and WFNA-9.

Effect of blending aromatic amines with triethylamine. - Not only are blends of aromatic amines with triethylamine more fluid at low temperatures than the aromatic amines alone (fig. 4), but in the case of N-ethylaniline and N,N-diethylaniline the blends tended to show more desirable ignition characteristics than either of the parent substances, as shown in the following table:

Fuel, percent by volume	Average igni	Average ignition-delay interval at $-40^{\circ}$ F, millisec						
in triethylamine	MA-2-17	RFNA-3-19	WFNA-7					
N-ethylaniline 50 N-ethylaniline 30 N-ethylaniline Triethylamine	51 45 48 No ignition	No ignition 54 36 755	No ignition Sporadic 105 Sporadic					
N,N-diethylaniline 50 N,N-diethylaniline 30 N,N-diethylaniline Triethylamine	90 35 65 No ignition	No ignition 42 33 755	No ignition 33 94 Sporadic					

Because of freezing temperatures higher than  $-40^{\circ}$  F, the ignition delays of pure primary aromatic amines were not determined in this investigation, but trends may be noted in a comparison of ignition delays at  $-40^{\circ}$  F of several 30 and 50 percent blends of aromatic amines in triethylamine, as shown in the following table:

Aromatic amine	Aromatic amine in	Average ignition-delay interval at -40° F millisec								
	triethyl- amine, percent by volume	MA-2-17	RFNA-3-19	WFNA-7	WFNA-9					
Aniline	50 30	33 38	27 21	44 23	102					
N-ethylaniline	50 30	45 48	54 36	Sporadic 105	Sporadic Sporadic					
N,N-diethylaniline	50 30	35 65	42	33 94	Sporadic Sporadic					
o-Toluidine	50 30	36 36	27 24	42 102	Sporadic Sporadic					
Xylidines	50 30	32 42	31 31	114 78	No ignition					

These data show that at  $-40^{\circ}$  F with mixed acid MA-2-17 the 50 percent blends of aromatic amines in triethylamine gave shorter average ignition delays, but with low-freezing red fuming nitric acid RFNA-3-19 the more fluid 30 percent blends gave shorter delays. No significant trend, however, was found with acids WFNA-7 and WFNA-9.

Fuels causing explosions. - Three other fuels showed short ignition delays at  $-40^{\circ}$  F with nitric acids containing 2 percent or less water, but, because they damaged the equipment with vigorous explosions, no further investigation was undertaken with this apparatus. These fuels were blends of 70 percent furfuryl alcohol plus 30 percent aniline (poor fluid characteristics), 56 percent furfuryl alcohol plus 24 percent aniline plus 20 percent methanol, and  $\alpha$ -furfuryl mercaptan. The  $\alpha$ -furfuryl mercaptan has shown satisfactory ignition with NA(anh)-0-3 and WFNA-2 at  $-40^{\circ}$  F in a 50-pound-thrust rocket chamber (ref. 12).

### Ignitibility of Blends of Aromatic Amines in Triethylamine with Red Fuming Nitric Acid Within Temperature

#### Range $70^{\circ}$ to $-105^{\circ}$ F

Ignition-delay characteristics of several blends of aromatic amines in triethylamine (table III) having viscosities less than 10 centistokes at -40° F were investigated with low-freezing red fuming nitric acid (RFNA-3-19) at several temperatures from 70° to -105° F and these data are shown in table IV. The reference fuel, a 50 percent blend of xylidines in triethylamine, was also investigated at several temperatures.

Effect of blending. - At several temperatures with RFNA-3-19 the 30 percent blends of several aromatic amines in triethylamine tended to give shorter ignition-delay intervals than the 50 percent blends, as shown in the following table:

Aromatic amine	Aromatic amine in triethyl-	e in millisec							
	amine, percent by volume)	70° F	-40° F	-76° F	-105° F				
Xylidines	50	27	31	56					
	30	19	31	49	No ignition				
N-ethylaniline	50	35	54	74	875				
,	30	26	36	61	664				
N,N-diethylaniline	50	36	42	70	No ignition				
	30	24	33	160	No ignition				

As has been previously noted, the same trend was shown for blends of other aromatic amines in triethylamine with RFNA-3-19 at  $-40^{\circ}$  F. The better ignitibility of the 30 percent blends is a practical advantage because these mixtures also have lower viscosities than the corresponding 50 percent blends (fig. 4).

Comparison of 30 percent blends of primary and secondary aromatic amines in triethylamine. - Because of the lower viscosities of the 30 percent blends, more of these blends were investigated. A comparison of the ignition delays of several 30 percent aromatic blends in triethylamine with RFNA-3-19 at several temperatures indicates that the 30 percent primary amine blends tend to ignite more readily than the 30 percent secondary and tertiary amine blends, as shown in the following table:

Aromatic amine, 30 percent by volume	Ave	Average ignition delay with RFNA-3-19, millisec							
in triethylamine	70° F	-40° F	-76° F	-87° F	-105° F				
Primary o-Toluidine Aniline Xylidines	19 21 19	24 21 31	38 37 49	61 108 148	210 > 1000 No ignition				
Secondary and tertiary N-ethylaniline N,N-diethylaniline	26 24	36 33	61 160		664 No ignition				

Of the fuels investigated, the blend of 30 percent o-toluidine in triethylamine appeared to have the most desirable ignition characteristics at low temperatures. (The data obtained at -105° F were with supercooled acid.)

Generalized temperature effects. - When Arrhenius type plots (log of average delay against reciprocal of absolute temperature) are made of the data for the aromatic anine blends (table IV), most of the curves show sharp breaks in the region of -76° F. At temperatures higher than about -76° F, the temperature coefficients are small, suggesting over-all activation energies from 0 to 2 kilocalories per mole. At lower temperatures, however, the variation with temperature is much higher, indicating over-all activation energies in a range from 10 to 40 kilocalories per mole.

A conjecture may be made that, at temperatures higher than approximately  $-76^{\circ}$  F, the ignition in the open-cup apparatus is limited only by simple G. N. Lewis type neutralization reactions, in these cases, probably the addition of nitronium  $(N0_2^+)$  and nitrosonium  $(N0^+)$  ions to the fuel molecules. The suggestion is made in reference 13 that these reactions are probably the first to occur because of their low activation energy. These addition reactions, which are equivalent to neutralization, can furnish heat for subsequent reactions that require higher activation energies. At lower initial temperatures, which under the condition of these experiments occur below approximately  $-76^{\circ}$  F, the possibility exists that other reactions or processes requiring higher activation energies are rate controlling.

Emphasis is placed on the fact, however, that the transition temperature (approx. -76° F) may apply only to the conditions of these experiments, since a transition at this temperature was not found in experiments made at the Lewis laboratory in a 50-pound-thrust rocket engine

using low-freezing nitric acids with 50 percent by volume N,N-dialylaniline plus triethylamine (ref. 12) and 30 percent o-toluidine plus triethylamine (ref. 14). The 50-pound-thrust-rocket experiments place even more confidence in these fuels by giving shorter ignition delays at very low temperatures. The NACA open-cup apparatus is shown to be a severe test for self ignitibility of rocket propellants at very low temperatures, and it is possible that other aromatic amine - triethylamine blends would show shorter delays at very low temperatures in an engine than in this apparatus.

Available direct comparisons (ref. 14) show that the numerical delays from the NACA open-cup apparatus break away from small-engine data as the viscosities of the propellants became greater than about 20 centistokes. Plots of log delay against log viscosity for most of the fuels from table IV show breaks occurring over a range of 10 to 40 centistokes. The fact that most of these breaks occur when the temperature is in the region of -76° F suggests the possibility that the breaks are associated with the acid. Since the viscosity of the acid would be about 20 centistokes at -76° F (ref. 12) and the volume of acid is three times the volume of the fuel, the criterion of approximate 20-centistokes seems at present to be as good as any for estimating where numerical ignition delays in the NACA open-cup apparatus depart from small-engine data.

#### Blends of Aromatic Amines plus $\alpha ext{-Furfuryl}$ Mercaptan

Experiments with blends of aromatic amines plus  $\alpha$ -furfuryl mercaptan (table IV) were discontinued because of inconsistent results probably caused by chemical changes which were noticeable after the mixture stood several days.

#### Practical Aspects

Low-freezing acid oxidants. - This work along with other research at the Lewis laboratory and elsewhere has helped in a reappraisal of red fuming nitric acid. New military specifications have been written for low freezing RFNA (ref. 15).

Low-temperature igniting fuels. - The fuels, which are indicated herein to be fluid and to ignite at low temperatures, could become important in an emergency if more recently developed fuels were in short supply.

#### SUMMARY OF RESULTS

An investigation was made of the fluid properties and ignition-delay characteristics of approximately 90 ruel-oxidant combinations at  $-40^{\circ}$  F and some of these combinations were investigated at several other temperatures within the range from  $70^{\circ}$  to  $-105^{\circ}$  F; the following results were obtained:

NACA TN 3884

l. Several acids were determined to have freezing temperatures less than  $-76^{\circ}$  F. Of these acids, the red fuming nitric acids containing approximately 3 percent water and 16 and 19 percent nitrogen tetroxide gave satisfactory ignition with several fuels at  $-40^{\circ}$  F.

- 2. Kinematic viscosities of aromatic amines were reduced by blending 50 and 30 percent by volume aromatic amine in triethylamine. Eight such blends had kinematic viscosities less than 10 centistokes at -40° F and less than 500 centistokes at -105° F. The blends were apparently nonideal solutions.
- 3. At -40° F, 11 blends of 30 and 50 percent aromatic amines, respectively, in triethylamine were found to give generally satisfactory ignition with mixed acid containing 2 percent water and 17 percent sulfuric acid and low-freezing red fuming nitric acid containing 3 percent water and 19 percent nitrogen tetroxide (average ignition-delay intervals from 20 to 65 millisec). All but two of these blends ignited with white fuming nitric acid containing 7 percent water with average delays varying from 23 to 115 milliseconds, but generally sporadic ignition was obtained with low-freezing white fuming nitric acid containing 9 percent water.
- 4. With mixed acid, red fuming nitric acid, and white fuming nitric acid at  $-40^{\circ}$  F, blends of 50 and 30 percent by volume of N-ethylaniline and N,N-diethylaniline, respectively, in triethylamine gave shorter average ignition delays than the unblended parent components.
- 5. Comparisons of blends, respectively, of 50 and 30 percent by volume aromatic amines in triethylamine showed that the 50 percent blends gave shorter ignition-delay intervals with mixed acid (2 percent water and 17 percent sulfuric acid) at  $-40^{\circ}$  F, but with red fuming nitric acid (approximately 3 percent water and 19 percent nitrogen tetroxide) the more fluid 30 percent blends gave shorter delay intervals at temperatures of  $70^{\circ}$ ,  $-40^{\circ}$ , and  $-76^{\circ}$  F.
- 6. Low-freezing red fuming nitric acid (approximately 3 percent water and 19 percent nitrogen tetroxide) gave the following average ignition delays with 30 percent by volume blends of aromatic amines in triethylamine (the acid had an approximate freezing temperature of -87° F and was supercooled at -105° F).

Aromatic amine, 30 percent by volume		Average ignition delay, millisec						
in triethylamine	70° F	-40° F	-76° F	-87° F	-105° F			
Primary o-Toluidine Aniline Xylidines	19 21 19	24 21 31	38 37 49	61 108 148	210 >1000 No ignition			
Secondary and tertiary N-ethylaniline N,N-diethylaniline	26 24	36 33	61 160		664 No ignition			

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, October 11, 1951

#### REFERENCES

- 1. Ladanyi, Dezso J., Sloop, John L., Humphrey, Jack C., and Morrell, Gerald: Starting of Rocket Engine at Conditions of Simulated Altitude Using Crude Monoethylaniline and Other Fuels with Mixed Acid. NACA RM E50D20, 1950.
- 2. Miller, Riley O.: Low-Temperature Ignition-Delay Characteristics of Several Rocket Fuels with Mixed Acids in Modified Open-Cup-Type Apparatus. NACA RM E50H16, 1950.
- 3. Anon.: Military Specification Fuel, Aircraft Turbine and Jet Engine Grades JP-3, JP-4, and JP-5. MIL-F-5624C, May 18, 1955.
- 4. Anon.: Military Specification Fuel, Aircraft and Jet Engine, Thermally Stable. MIL-F-25524 (USAF), Feb. 3, 1956.
- 5. Bartlett, P. M.: Recommended Upper Air Standard Temperatures for Aeronautical Use. Power Plant Memo. No. 26, Navy Dept., Bur. Aero.
- 6. Warner, B. F.: Studies in Self-Igniting Liquid Propellants. Pt. II. Ignition Delays of Propellants Based on Nitric Acid-Aniline. Rep. No. 201/R/47, Chem. Res. & Dev. Dept., British M.O.S., Nov. 1946.

NACA TN 3884

7. Anon: Air Force-Navy Aeronautical Specification Acid; Nitric, White Fuming, No. 14104, Mar. 15, 1948.

- 8. Anon:: Federal Specification Lubricants, Liquid Fuels, and Related Products; Methods of Inspection, Sampling, and Testing. Method 30.5.1, B, VV-L-791d, Nov. 15, 1948. (Available from Supt. of Documents.)
- 9. Sanderson, R. T.: Viscosity-Temperature Characteristics of Hydrocarbons. Ind. and Eng. Chem., vol. 41, no. 2, Feb. 1949, pp. 368-374.
- 10. Glasstone, Samuel: Textbook of Physical Chemistry. D. Van Nostrand Co., Inc., 1940.
- 11. Fuchs: Die Amine als Raketentriebstoffe. ER Bericht Nr. 135, BMW-Flugmotorenbau G.m.b.H., Berlin-Spandau, June 1, 1943. (ATI No. 26958.)
- 12. Ladanyi, Dezso J.: Ignition Delay Experiments with Small-Scale Rocket Engine at Simulated Altitude Conditions Using Various Fuels with Nitric Acid Oxidants. NACA RM E51J01, 1952.
- 13. Miller, Riley O.: Effects of Nitrogen Tetroxide and Water Concentration on Freezing Point and Ignition Delay of Fuming Nitric Acid. NACA RM E53G31, 1953.
- 14. Ladanyi, Dezso, J., and Miller, Riley O.: Comparison of Ignition Delays of Several Propellant Combinations Obtained with Modified Open-Cup and Small-Scale Rocket Engine Apparatus. NACA RM E53D03, 1953.
- 15. Anon.: Military Specification Nitric Acid, Fuming Technical. MIL-N-7254B, Feb. 14, 1955.
- 16. Carpenter, Clifford D., and Lehrman, Alexander: The Solid-Liquid Temperature Relation in the Ternary System H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>-H<sub>2</sub>O and Its Relation to the Ternary System N<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O-SO<sub>3</sub>. Trans. Am. Inst. Chem. Eng., vol. 17, pt. 1, 1925, pp. 35-73.
- 17. Washburn, Edward W., ed.: International Critical Tables. Vols. III and IV. McGraw-Hill Book Co., Inc., 1928.

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TABLE I - DESCRIPTION OF ACIDS USED IN IGNITION EXPERIMENTS

					by weight		
Code designation	Approximate freezing temperature,	acid,	Sulfuric acid, H <sub>2</sub> SO <sub>4</sub>	Nitrogen tetroxide, N <sub>2</sub> O <sub>4</sub>	Water, H <sub>2</sub> O (by difference)	Other	Remarks
Mixed acids							
MA-5-15		80.0	15.3		4.7		Prepared from chemically pure white fuming nitric
MA-2-17	-68	81.3	17.1		1.6		acid and oleum (ref. 2).  Prepared from commercial white fuming nitric acid (received from manufacturer in glass bottles)
MA-4-17		79.4	16.7		3.9		and chemically pure cleum.  A commercial mixed acid supplied by Bureau of Aeronautics, Department of the Navy
MA-0-29	a_87	71.0	29.0				(ref. 2). Prepared from commercial white fuming nitric acid (aluminum drum) and chemically pure oleum. Composition calculated.
Red fuming nitric acids							
RFNA-3-16	-82	80.8		15.8	3.4		Prepared by mixing commercial white fuming nitric acid (aluminum drum) and chemically pure red
RFNA-3-19(lot a)	-87	78.0		19.0	3.0		fuming nitric acid.  Prepared by mixing commercial anhydrous nitric acid (aluminum drum) and chemically pure red fuming
(lot b)	-87 -87	78.5 78.8		18.8 19.0	2.7		nitric acid. Prepared in same manner as lot a. Prepared by slow addition of water to chemically pure anhydrous red fuming nitric acid at low
RFNA-3-29 RFNA-5-35	-68	67.6 60.1		29.2 34.7	3.2 5.2		temperature. A chemically pure red fuming nitric acid. A chemically pure red fuming nitric acid.
White fuming nitric acids							
NA(anh)-0-3	-45	97.1		2.6	0.3		A commercial acid supplied in an aluminum drum, but
WFNA-2	-45	97.7		0.5	1.8		stored in pyrex glass shortly after receipt. A commercial acid supplied and stored in an aluminum
WFNA-7	-69	93.0		0.2	6.8		drum. A chemically pure acid stored about 2 years in soft
WFNA-9	-81	91.1		0.2	8.7		glass bottles. Prepared by slow addition of water to WFNA-7 at -40° F. Composition calculated.
Acids containing nitrate salts							
WFNA-2(5-NH <sub>4</sub> NO <sub>3</sub> )	-54	92.8		0.5	1.7	5.0 ammonium nitrate	Prepared by dissolving ammonium nitrate in WFNA-2.
WFNA-2(10-NH4NO3)	b-23	87.9		0.5	1.6	10.0 ammonium nitrate	Composition calculated. Prepared as above. Composition calculated.
WFNA-8(6-KNO <sub>3</sub> )	-96	85.9		0.4	7.7	6.0 potassium nitrate	Prepared by addition of potassium nitrate and water to commercial white fuming nitric acid. Composition calculated.
Acids containing perchloric acid							
WFNA-9(7-HClO <sub>4</sub> )	-78	83.9		c <sub>0.4</sub>	9.0	6.7 perchloric acid	Prepared by addition of 70 percent perchloric acid and water to commercial white fuming nitric acid.
WFNA-11(4-HC10 <sub>4</sub> )	-91	85.0		c 0.4	10.5	4.1 perchloric acid	Composition calculated. Prepared as above. Composition calculated.

aData of ref. 16.

bGreater portion of solids melted as temperature increased to -61° F.

cColorless solution indicates nitrogen tetroxide - nitrogen dioxide not present in free state.

NACA TN 3884

TABLE II - IGNITION STUDY AT  $-40^{\circ}$  F OF SEVERAL NITRIC ACID OXIDANTS WITH TWO 50-50 (BY VOLUME) BLENDS OF AROMATIC AMINE PLUS TRIETHYLAMINE

[DAA, N,N-diallylaniline;  $T_{\rm f}$ , approximate freezing temperature,  ${}^{\rm O}F$ .]

Acid oxidant composition, percent by weight	Fuel in triethylamine, 50 percent by volume	Number of trials	10			mi nt re	llisec	al at -40 ts averag	ge]	600	1000
Mixed acids		,	10		T						
MA-2-17 (T <sub>f</sub> , -68) 81.3 HNO <sub>3</sub> -17.1 H <sub>2</sub> SO <sub>4</sub> -1.6 H <sub>2</sub> O	Xylidines DAA	3 4			-						
MA-0-29 (T <sub>f</sub> , -87) <sup>a</sup> 70.7 HN0 <sub>3</sub> -29.3 H <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	Xylidines DAA	4 3				0					
Red fuming nitric acids											
RFNA-3-16 (T <sub>f</sub> , -82) 80.8 HNO <sub>3</sub> -15.8 N <sub>2</sub> O <sub>4</sub> -3.4 H <sub>2</sub> O	Xylidines DAA	4		-							
RFNA-3-19 (lot a)(T <sub>f</sub> , -87) 78.0 HNO <sub>3</sub> -19.0 N <sub>2</sub> O <sub>4</sub> -3.0 H <sub>2</sub> O	Xylidines DAA	5 4	_		-						
RFNA-3-29 (T <sub>f</sub> , -68) 67.6 HNO <sub>3</sub> -29.2 N <sub>2</sub> O <sub>4</sub> -3.2 H <sub>2</sub> O	Xylidines	3		-	0						
RFNA-5-35 60.1 HNO <sub>3</sub> -34.7 N <sub>2</sub> O <sub>4</sub> -5.2 H <sub>2</sub> O	Xylidines DAA	4 4			-0-	0					

White fuming nitric acids			10	20	40	60	100	200	400	600	1000
white luming hitric acids											
$NA(anh)-0-3 (T_f, -45)$	Xylidines	10			0						
97.1 HNO <sub>3</sub> -2.6 N <sub>2</sub> O <sub>4</sub> -0.3 H <sub>2</sub> O	DAA	4	-	0-							
WFNA-2 (T <sub>f</sub> , -45)	Xylidines	°6			0						-
97.7 HN03-0.5 N <sub>2</sub> O <sub>4</sub> -1.8 H <sub>2</sub> O	DAA	6	-	-							
WFNA-7 (T <sub>f</sub> , -69)	Xylidines	8					1	-(Weak)			
93.0 HNO <sub>3</sub> -0.2 N <sub>2</sub> O <sub>4</sub> -6.8 H <sub>2</sub> O	DAA	2							No	ignit:	ion →
WFNA-9 (T <sub>f</sub> , -81)	Xylidines	2							No	ignit	ion -
91.1 HNO <sub>3</sub> -0.2 N <sub>2</sub> O <sub>4</sub> -8.7 H <sub>2</sub> O <sup>b</sup>											
Special acids											
WFNA-2(5-NH <sub>4</sub> NO <sub>3</sub> ) (T <sub>f</sub> , -54)	Xylidines	3					-	_			
92.8 HNO3-5.0 NH4NO3											
-0.5 N <sub>2</sub> O <sub>4</sub> -1.7 H <sub>2</sub> O <sup>b</sup>											
WFNA-2(10-NH <sub>4</sub> NO <sub>3</sub> ) (T <sub>f</sub> , -23)	Xylidines	4						0			
87.9 HNO3-10.0 NH <sub>4</sub> NO <sub>3</sub>											
-0.5 N <sub>2</sub> O <sub>4</sub> -1.6 H <sub>2</sub> O <sup>b</sup>											
WFNA-8(6-KNO3) (T <sub>f</sub> , -96)	Xylidines	2							No	ignit	ion-
85.9 HNO <sub>3</sub> -6.0 KNO <sub>3</sub>											
-7.7 H <sub>2</sub> 0-0.4 N <sub>2</sub> 0 <sub>4</sub>											
WFNA-9 (7-HClO <sub>4</sub> ) (T <sub>f</sub> , -78)	Xylidines	2							No	ignit	ion-
83.9 HNO <sub>3</sub> -6.7 HClO <sub>4</sub> -9.0 H <sub>2</sub> O <sup>b</sup>											
WFNA-11(4-HClO <sub>4</sub> ) (T <sub>f</sub> , -91)	Xylidines	2							No	ignit	ion
85.0 HNO <sub>3</sub> -4.1 HClO <sub>4</sub> -10.5 H <sub>2</sub> O <sup>b</sup>								May Park			

aData from ref. 16. bCalculated approximate composition. cIgnition delays from electronic timer only.

TABLE III - IGNITION STUDY AT -40° F OF VARIOUS FUELS WITH SEVERAL NITRIC ACID OXIDANTS [Symbols for acid oxidants are designated in table I;  $\nu$ , kinematic viscosity of fuel at -40° F, centistokes]

Fuel, percent by volume	Acid oxidant	Number of trials	Ignition-delay interval at -40° F, millisec								
percent by volume	021144110	01 011415	[Data point represents average]								
			10 20 40 60 100 200 400 600 1000								
Aromatic and aliphatic amines											
50-Aniline - 50-triethylamine ( $\nu$ , 30.1)	MA-2-17 RFNA-3-19(lot c) WFNA-7 WFNA-9	4 4 4 4	-0								
30-Aniline - 70-triethylamine (ν, 8.45)	MA-2-17 RFNA-3-19(lot a) WFNA-7 WFNA-9	4 4 4 4	(Weak)								
N-Ethylaniline ( $\nu$ , 44)	MA-2-17 RFNA-3-19(lot c) WFNA-7	a <sub>6</sub> 2 2	No ignition—								
50-N-Ethylaniline - 50-triethylamine ( $\nu$ , 7.39)	MA-2-17 RFNA-3-19(lot a) WFNA-7 WFNA-9	4 4 4 4	(1 of 4 ignited)								
30-N-Ethylaniline - 70-triethylamine ( $\nu$ , 3.40)	MA-2-17 RFNA-3-19(lot a) WFNA-7 WFNA-9	4 4 4 4	(3 of 4 ignited)								
N,N-Diethylaniline $(\nu, 37.5)$	MA-2-17 RFNA-3-19(lot a) WFNA-7	4 2 2	No ignition— No ignition—								
50-N,N-Diethylaniline - 50-triethylamine ( $\nu$ , 3.75)	MA-2-17 RFNA-3-19(lot c) WFNA-7 WFNA-9	4 6 4 4	(1 of 4 ignited)								
30-N,N-Diethylaniline - 70-triethylamine ( $\nu$ , 2.18)	MA-2-17 RFNA-3-19(lot c) WFNA-7 WFNA-9	4 4 4 4	(1 of 4 ignited)								
50-N, N-Diallylaniline - 50-triethylamine ( $\nu$ , 4.92)	MA-2-17 RFNA-3-19(lot a) WFNA-7	5 4 2	No ignition-								
50-o-Toluidine - 50-triethylamine ( $\nu$ , 19.8)	MA-2-17 RFNA-3-19(lot c) WFNA-7 WFNA-9	4 4 4 4	(3 of 4 ignited)								
30-o-Toluidine - 70-triethylamine ( $\nu$ , 5.69)	MA-2-17 RFNA-3-19(lot a) WFNA-7 WFNA-9	4 4 4 4	-O- (3 of 4 ignited)								

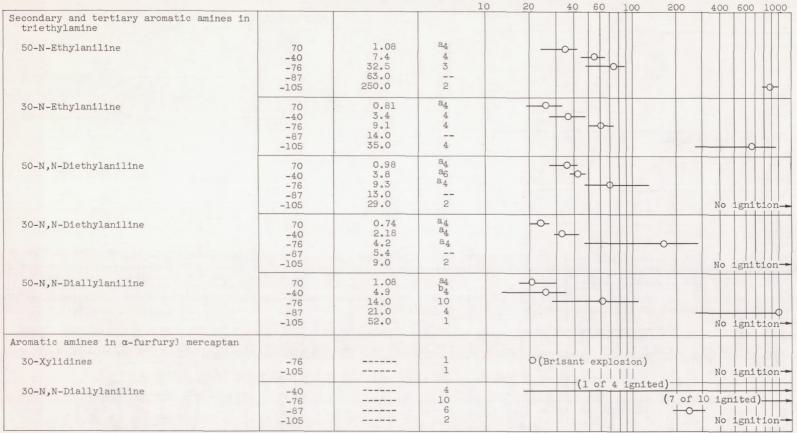
50-Xylidines - 50-triethylamine (v, 17.5)	MA-2-17	6	10	20	40 6		00 200	400 600 100
	RFNA-3-19(lot b) WFNA-7 WFNA-9	5 8 2					(Weak)	No ignition_
30-Xylidines - 70-triethylamine ( $\nu$ , 4.85)	MA-2-17 RFNA-3-19(lot a) WFNA-7 WFNA-9	4 7 4 4		-		-0-	(Weak)	
Crude monoethylaniline ( $\nu$ , 90)	MA-2-17 WFNA-7	a <sub>8</sub>				0		No ignition -
Triethylamine ( $\nu$ , 1.13)	MA-2-17 RFNA-3-19(lot c) WFNA-7	2 2 2					(1 of	No ignition_ 2 ignited)
Diethylenetriamine	MA-2-17 WFNA-7	a <sub>4</sub> 2					0 101	No ignition-
iscellaneous fuels								
70-Furfuryl alcohol - 30-xylenes ( $\nu$ , 51)	MA-5-15 NA(anh)-0-3 WFNA-7	a7 a7 a8		-	-0		-	of 8 ignited)
Tetrahydrofuran	MA-2-17 WFNA-7	a <sub>2</sub>				1	(1	of 2 ignited) No ignition-
3-Mercapto-1-propanol	MA-2-17	a4						No ignition-
Mixed butyl mercaptans $(\nu, 1.3)$	MA-4-17 WFNA-2	a <sub>8</sub> a <sub>10</sub>	-	-			(5 of 10 igr	
Allyl glycidyl ether (v, 6.15)	MA-2-17	a <sub>4</sub>	-				(3 of	4 ignited)
2-Methylpentadienes (contained inhibitor) ( $\nu$ , .94)	MA-2-17 WFNA-7	a <sub>4</sub> 2				0		No ignition-
50-2-Methylpentadienes - 50- <u>n</u> -heptane	MA-2-17	2					W	No ignition-
2,2,4,6-Tetramethyldihydropyridine ( $\nu$ , 26.7)	MA-2-17 WFNA-7	a <sub>4</sub> 4						No ignition-
l-Vinylcyclohexene-3	MA-2-17 WFNA-2	2 2						No ignition- No ignition-
Gum turpentine ( $\nu$ , 8.8)	MA-5-15 RFNA-3-19(lot c) WFNA-2	a <sub>3</sub> 2 4				0		No ignition- No ignition-
Hydrazine hydrate	MA-5-15 WFNA-2	b <sub>4</sub> 4						No ignition-

aData from electronic timer. bTemperature, -4° F.

TABLE IV - STUDY AT SEVERAL TEMPERATURES OF VISCOSITIES AND IGNITION OF VARIOUS FUEL BLENDS WITH LOW-FREEZING RED FUMING NITRIC ACIDS CONTAINING APPROXIMATELY 3 PERCENT WATER AND 19 PERCENT NITROGEN TETROXIDE

[All ignition data are with RFNA-3-19(lot a) except as noted and all acids had freezing temperature of approximately  $-87^{\circ}$  F and were supercooled at  $-105^{\circ}$  F.]

Fuel, percent by volume	Temperature,	Fuel kinematic viscosity (fig. 4), centistokes	Number of trials	Ignition-delay interval millisec [Data point represents average]								
				10	20	40	60	100	200	400	600	1000
Primary aromatic amines in triethylamine 30-Aniline	70 -40 -76 -87 -105	1.07 8.5 45.0 95.0 480.0	a <sub>4</sub> 4 4 6 2		00	0		-0-				0
30- <u>o</u> -Toluidine	70 -40 -76 -87 -105	1.01 5.7 19.5 34.0 110.0	a4 4 4 4		-0-0-	-0-						
50-Xylidines	70 -40 -76	1.52 17.5 138.0	a4 5 6									
30-Xyl1dines	70 -40 -76 -87 -105	0.96 4.9 16.0 27.0 80.0	a <sub>4</sub> b <sub>7</sub> 5 6		0 -		<u> </u>	-	· .	No	ignit	ion-



 $^{\rm aRFNA-3-19}({\rm lot~c})$  used to determine ignition delays.  $^{\rm bRFNA-3-19}({\rm lot~b})$  used to determine ignition delays.

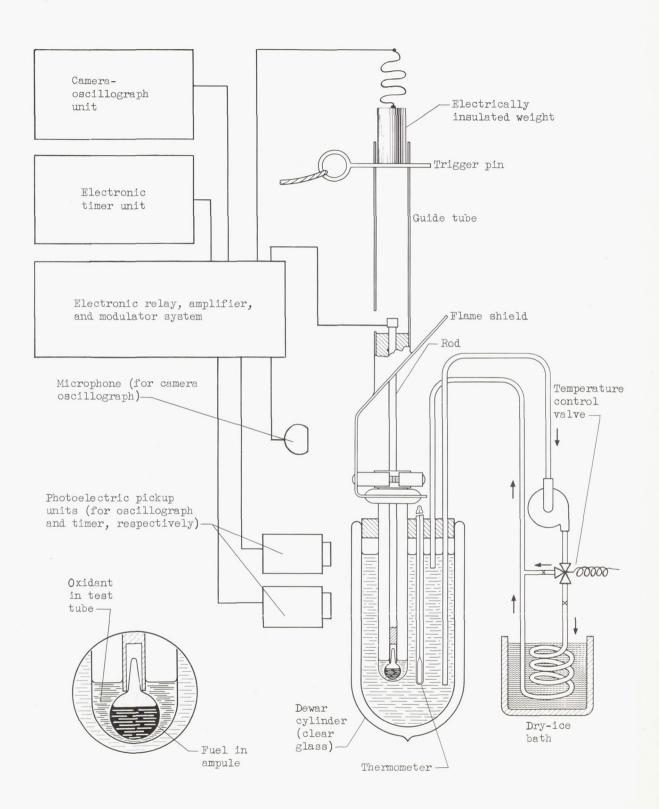
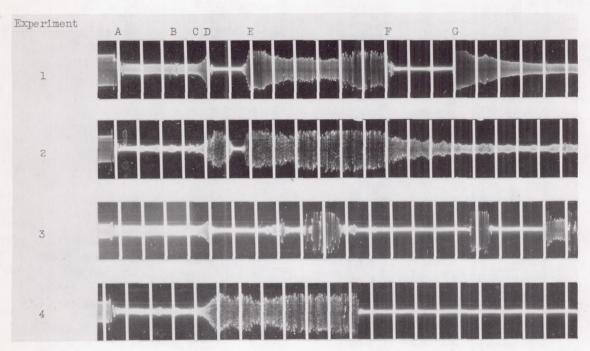
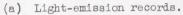
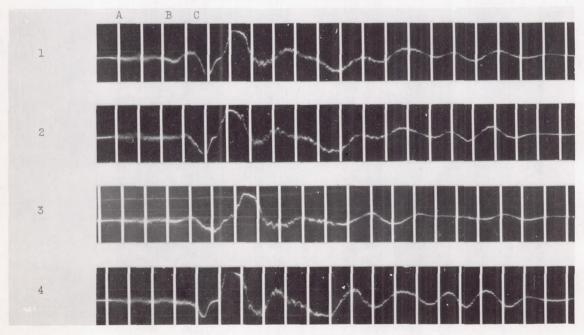


Figure 1. - Ignition-delay apparatus.

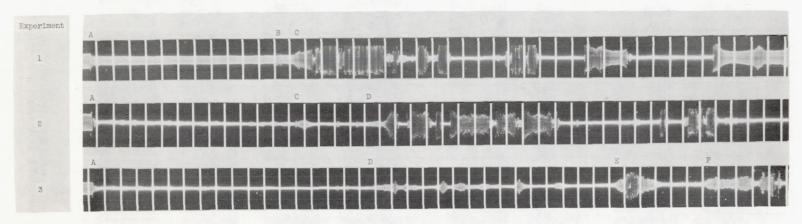




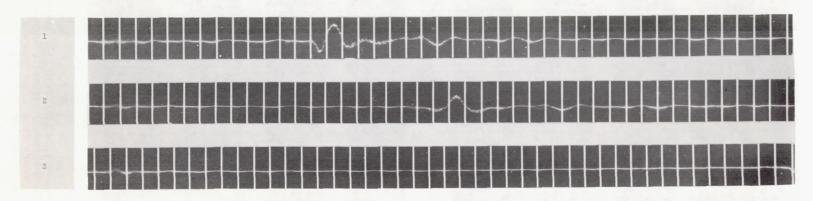


(b) Sound records.

Figure 2. - Oscillograph records of light emission and sound from ignition of a blend of 30 percent aniline plus 70 percent triethylamine with RFNA-3-19 (lot a) at  $-76^{\circ}$  F.

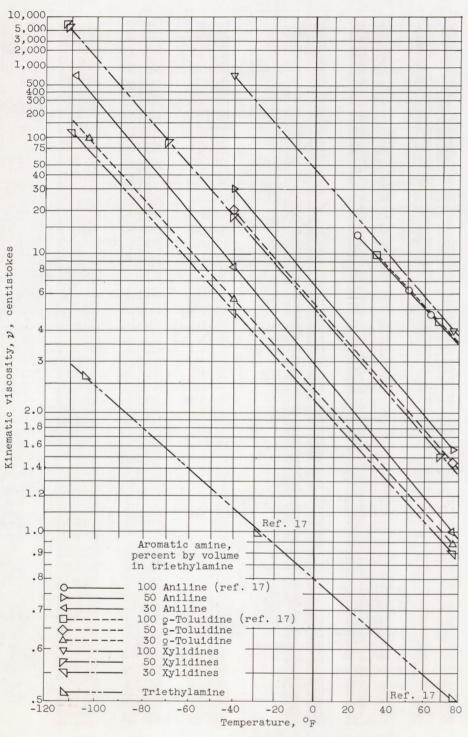


(a) Light-emission records.



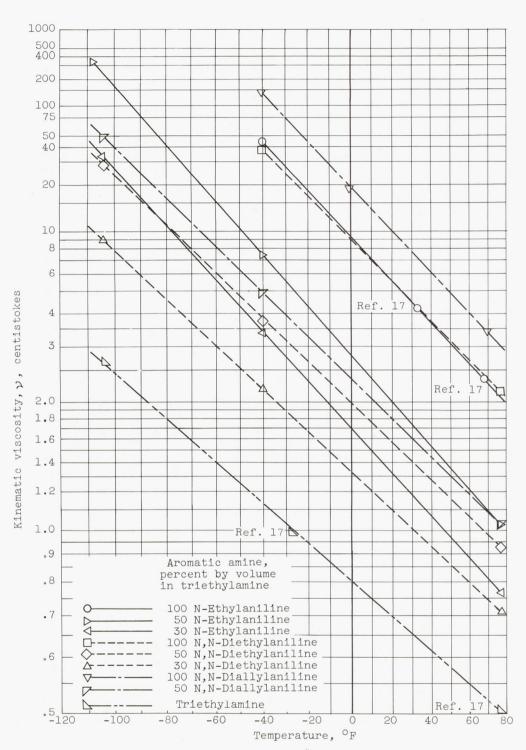
(b) Sound records.

Figure 3. - Oscillograph records of light emission and sound from ignition of a blend of 30 percent xylidine plus 70 percent triethylamine with RFNA-3-19 (lot a) at -87° F.



(a) Primary amines.

Figure 4. - Kinematic viscosities of aromatic amines, triethylamine, and blends of aromatic amines in triethylamine as functions of temperature. (Coordinate scales similar to those recommended by A.S.T.M.; see ref. 9.)



(b) Secondary and tertiary amines.

Figure 4. - Concluded. Kinematic viscosities of aromatic amines, triethylamine, and blends of aromatic amines in triethylamine as functions of temperature. (Coordinate scales similar to those recommended by A.S.T.M.; see ref. 9.)